[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO METHYL TIN DERIVATIVES. V. ACTION OF SODIUM TRIMETHYL TIN ON METHYLENE CHLORIDE

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A. Di-Trimethylstannylmethane

Kraus and Greer[1] studied the action of methylene chloride on disodium dimethyl tin and found that the organic group combines with the dimethyl tin group to form a compound that has a marked tendency to polymerize. Kraus and Sessions[2] treated sodium trimethyl tin with symmetrical ethylene chloride. The products of reaction proved to be sodium chloride, trimethyl tin and ethylene. It seemed worth while to study the corresponding reaction between sodium trimethyl tin and methylene chloride in liquid ammonia. This reaction might be expected to proceed according to the equation

$$2(CH_3)_3SnNa + CH_2Cl_2 = [(CH_3)_3Sn]_2CH_2 + 2NaCl$$

Experiment showed that reaction takes place quantitatively, as was anticipated, but in attempting to characterize the compound by its reaction with sodium in liquid ammonia, certain unexpected reactions occurred. These were followed up further and are described in the next section.

Preparation.—A quantity of trimethyl tin bromide was dropped slowly into several hundred cubic centimeters of liquid ammonia contained in a Dewar flask. Sodium was then added until the compound was completely reduced to a sodium trimethyl tin. The end-point of the reaction is indicated by the appearance of a permanent blue color due to free sodium.

On now adding methylene chloride to the solution of sodium trimethyl tin, immediate reaction occurred with the formation of a liquid precipitate. When the reaction was completed, the supernatant liquid was colorless. The ammonia was allowed to evaporate and the oil was washed several times with distilled water, from which it was then separated. It was dried by filtering through anhydrous sodium sulfate in an atmosphere of nitrogen. Samples of the oil were introduced into weighed tubes and sealed under an atmosphere of nitrogen.

Analyses and Molecular Weight.—The compound was analyzed for tin by the Carius method. Subs. 0.3865, 0.6605, 0.6941: SnO_2, 0.3451, 0.5841, 0.6120. Calcd. for $[(CH_3)_3Sn]_2CH_2$: Sn, 69.50. Found: Sn, 70.33, 69.66, 69.45. The molecular weight was determined in benzene by the freezing-point method: solvent, 17.66, 20.85; solute, 0.7387, 0.9903; Δt, 0.590, 0.682°; mol. wt. found, 354.6, 348.2. Calcd. for $[(CH_3)_3Sn]_2CH_2$: 341.6.

Properties.—Di-trimethylstannylmethane is a colorless liquid which is quite fluid at liquid ammonia temperatures. It boils at 199–201° under normal pressure.

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[1] Kraus and Greer, THIS JOURNAL, **47**, 2568 (1925).

[2] Kraus and Sessions, *ibid.*, **47**, 2361 (1925).

The compound is readily iodized in benzene or chloroform solution. In two experiments 2.1 and 1.99 moles of iodine were required per mole of the compound. Reaction thus takes place according to the equation

$$[(CH_3)_3Sn]_2CH_2 + 2I_2 = 2(CH_3)_3SnI + CH_2I_2$$

After iodination in chloroform, the trimethyl tin iodide was precipitated by means of ammonia. Analysis of the product showed that it consisted of the ammonia complex $(CH_3)_3SnI\cdot NH_3$. From the filtrate there was obtained a product melting unsharply at 2°. This was evidently impure methylene iodide, which melts at 5.7°.

B. Action of Sodium on Di-Trimethylstannylmethane and Allied Reactions

In order to establish further the constitution of the compound whose preparation has been described in the preceding section, it was reduced with sodium in liquid ammonia and the resulting products were studied. In general, when a metallo-organic compound of the type R_4M is reduced with sodium in liquid ammonia, the following reaction occurs

$$R_4M + 2Na + NH_3 = R_3MNa + NaNH_2 + RH \qquad (I)$$

Reaction might also be expected to occur according to the equation

$$2R_4M + 2Na = 2R_3MNa + R_2 \qquad (II)$$

However, this latter reaction occurs infrequently, except when one of the substituents R is hydrogen.

Preliminary Experiments.—A weighed quantity of di-trimethylstannylmethane was treated with sodium in liquid ammonia. The metal was introduced, a little at a time, until the reduction was completed and the amount of sodium added was determined by weighing back. Gas evolved in the course of the reduction was collected over water and its volume and density were determined. Ammonium bromide was then added to the reaction mixture and the gas evolved in this reaction was collected over water and its volume and density were determined.

It was anticipated that, in the initial process of reduction, reaction would occur according to the equation

$$[(CH_3)_3Sn]_2CH_2 + 4Na + 2NH_3 = 2(CH_3)_3SnNa + 2NaNH_2 + CH_4 \qquad (III)$$

Since sodium amide is difficultly soluble in liquid ammonia, it was expected that it would be precipitated. A precipitate of sodium amide was, in fact, formed as the reaction proceeded. On adding ammonium bromide to the products of this reaction, it was anticipated that the sodium amide would be neutralized by the ammonium bromide, according to the equation

$$NaNH_2 + NH_4Br = NaBr + 2NH_3 \qquad (IIIA)$$

while the sodium trimethyl tin should be converted to the stannane, according to the equation

$$(CH_3)_3SnNa + NH_4Br = NaBr + (CH_3)_3SnH + NH_3$$

Two reactions were carried out in which, respectively, 6.4 and 6.8 m. moles of di-trimethylstannylmethane were treated with 21.6 and 23.2 m. atoms of sodium and 94.2

and 101.9 (4.2 and 4.6 m. moles) cc. of gas were evolved. The density of the gas indicated a mean molecular weight of 19.6 and 18.8, respectively. In the two experiments, 3.6 and 3.4 m. atoms of sodium were required per mole of compound in order to complete the reduction. According to Equation III, 4 atoms of sodium are required per mole of compound. The discrepancy is probably due to loss of the original material, which is appreciably volatilized in the course of the process of reduction. The molecular weight of the gas indicated that it was probably methane.

On adding ammonium bromide to the product of the above reductions, the solid (sodium amide) dissolved and a gas was evolved. In the two experiments, respectively, 12.7 and 14.1 m. moles of ammonium bromide were required to complete the initial stage of the reaction. This is approximately 2 moles of ammonium bromide per mole of the original compound. The density of the evolved gas in the two experiments corresponded to a molecular weight of 10.3 and 14.0, indicating that it consisted of hydrogen admixed with an impurity. On disappearance of the solid precipitate, a clear yellow solution remained. It was inferred that this color was due to sodium trimethyl tin. On further addition of ammonium bromide, no gas was evolved and a liquid was precipitated while the yellow color disappeared. The liquid proved to be trimethylstannane.

The appearance of hydrogen on addition of ammonium bromide to the products of reduction was unexpected. If ammonium bromide reacted with sodium amide according to Equation IIIA, no hydrogen would be produced, while any ammonium bromide reacting with sodium trimethyl tin is known to form trimethylstannane. The reaction between sodium amide and trimethylstannane has not been previously studied. It is known, however, that the alkali metal amides react readily with triphenylmethane according to the equation

$$(C_6H_5)_3CH + NaNH_2 = (C_6H_5)_3CNa + NH_3$$

Since sodium trimethyl tin is highly soluble and sodium amide is only sparingly soluble in liquid ammonia, it is to be expected that, on adding ammonium bromide to a mixture of the two in liquid ammonia, trimethylstannane would first be formed and that this compound would then react with the sodium amide present. Accordingly, it was found necessary to study the action of sodium amide on trimethylstannane.

The high values found for the molecular weights of the gases produced in the reactions described above indicated that volatile tin compounds were carried over with the escaping gases. Kraus and Sessions[2] found this to be the case in the reduction of tetramethyl tin. Accordingly, in subsequent experiments the evolved gases were passed through a strong solution of sodium in liquid ammonia, prior to collecting them over water. In order to establish the nature of the reduction process in the case of di-trimethylstannylmethane, the reaction between trimethylstannane and sodium amide was first studied. To establish the nature of this reaction fully, it was found necessary to study also the reaction between sodium amide and trimethyl tin. Finally, the reduction of di-trimethylstannylmethane was repeated and the products of reaction were identified.

Action of Sodium Amide on Tri-methylstannane.—A known weight of trimethyl tin bromide was introduced into a reaction tube and dissolved in liquid ammonia. The bromide was reduced to sodium trimethyl tin by means of sodium and this, in turn, was converted to trimethylstannane by addition of an equivalent quantity of ammonium bromide. To this preparation sodium amide was added until reaction was complete. Gas was evolved throughout this reaction; it was collected over water and its density determined. In a second experiment the evolved gas was passed through a solution of sodium in liquid ammonia prior to collecting over water.

In two experiments, respectively, 15.4 and 15.4 m. moles of trimethylstannane were treated with 20.8 and 14.3 m. moles of sodium amide with the evolution of 4.35 and 2.06 m. moles of gas. The density of the gas in the first reaction, collected directly over water, corresponded to a molecular weight of 28.1, while that of the second reaction washed through a sodium solution was 4.80. Because of the low solubility of sodium amide, an excess of this substance was added in both experiments in order to complete the reaction, and the proportion of this material to the stannane is without significance. However, in the first experiment, 0.28 mole of gas was evolved per mole of stannane, and in the second only 0.13 mole. Seemingly, several reactions occur in varying proportions, depending upon the conditions of the experiment. That the evolved gas was hydrogen is clearly shown by the low value of the molecular weight in the second experiment.

The reactions may be formulated as follows

$$(CH_3)_3SnH + NaNH_2 = (CH_3)_3SnNa + NH_3 \qquad (IV)$$

$$2(CH_3)_3SnH + NaNH_2 = (CH_3)_3SnNa + (CH_3)_3SnNH_2 + H_2 \qquad (V)$$

The proportion in which the two reactions take place probably depends upon the concentration and state of subdivision of the reacting materials.

Sodium amide is only slightly soluble in liquid ammonia, and in order to obtain a quantity of this material in a finely divided condition, the preceding experiment was repeated with some modification. Tetramethyl tin was treated with an equivalent quantity of metallic sodium. According to Kraus and Sessions,[2] this reaction leads to the formation of a solution of sodium trimethyl stannide and a finely divided precipitate of sodium amide in equivalent amount. Ammonium bromide was added to the resulting solution. Because of the relatively low solubility of sodium amide, and perhaps for other reasons, the ammonium bromide initially reacts with sodium trimethyl stannide to form trimethylstannane, which, in turn, reacts with sodium amide. The gas evolved, on addition of ammonium bromide, was passed through a concentrated solution of sodium in liquid ammonia prior to collecting it over water.

In this reaction 11.9 m. moles of tetramethyl tin were treated with 23.8 m. atoms of sodium, which resulted in the production of a solution containing 11.9 m. moles of sodium trimethyl stannide and 11.9 m. moles of finely divided sodium amide. This was treated with 13.3 m. moles of ammonium bromide; 83.0 cc. of gas was evolved, having a mean molecular weight of 5.01. The volume of gas corresponded to 3.7 m. moles, or 7.4 m. atoms of hydrogen. Therefore, 62% of the stannane formed in the course of the reaction was converted to sodium trimethyl stannide and trimethyl tin amine, according to Equation V.

The isolation of trimethyl tin amine involves many difficulties and its presence was accordingly shown by certain characteristic reactions. When sufficient ammonium bromide had been added to the initial reduction product to react with all the sodium amide, the solution, which was now transparent and of a pale yellow color, was treated with sodium. No gas was evolved but a finely divided precipitate was formed having the characteristics of sodium amide. Reaction occurred according to the equation

$$(CH_3)_3SnNH_2 + 2Na = (CH_3)_3SnNa + NaNH_2 \qquad \text{(VI)}$$

In order to show that the precipitate formed in this reaction was sodium amide, the mixture was treated with ammonium bromide. This was thus a repetition of Reaction V. On addition of ammonium bromide, a gas was evolved, and this evolution of gas continued until the precipitate had disappeared. This behavior is characteristic of a mixture of sodium trimethyl stannide and sodium amide. Further addition of ammonium bromide caused precipitation of trimethyl stannane.

Basing our calculation on the amount of hydrogen evolved in the preceding reaction, there were present in the solution 3.7 m. moles of trimethyl tin amine. To this solution were added 6.8 m. atoms of sodium and, on addition of excess ammonium bromide, there was evolved 31.8 cc. of gas, or 1.42 m. moles, having a mean molecular weight of 4.6. The amount of gas evolved corresponds to a reaction in which 75% of the product, formed according to Equation VI, reacted according to Equation V when ammonium bromide was added.

On adding ammonium bromide to a solution of sodium trimethyl stannide, in the presence of sodium amide, reaction takes place, initially according to the equation

$$(CH_3)_3SnNa + NH_4Br = (CH_3)_3SnH + NaBr + NH_3 \qquad \text{(VII)}$$

The trimethylstannane resulting from this reaction then reacts to the extent of about 70% according to Equation V, and 30% according to Equation IV.

Action of Sodium Amide on Trimethyl Tin.—In order to obtain some further data relative to trimethyl tin amine, the reaction between trimethyl tin and sodium amide was studied. Owing to the low solubility of both constituents in liquid ammonia, reaction takes place slowly according to the equation

$$[(CH_3)_3Sn]_2 + NaNH_2 = (CH_3)_3SnNa + (CH_3)_3SnNH_2 \qquad \text{(VIII)}$$

A slight excess of sodium amide was added in order to ensure completion of the reaction. The resulting solution exhibited the characteristic yellow color of sodium trimethyl stannide. Since trimethyl tin amine is volatile, its presence was shown by evaporating the ammonia solution into water, acidifying the aqueous solution with sulfuric and nitric acids and evaporating to dryness. As the result of this procedure, a small quantity of stannic oxide was obtained, indicating that a volatile tin compound was carried over with the ammonia vapors. In another experiment the ammonia was recondensed and sodium was added to the condensate. Immediate reaction took place, the solution acquired a yellow color, characteristic of sodium trimethyl stannide, and a finely crystalline precipitate was formed which resembled sodium amide. These observations would seem to demonstrate the presence of trimethyl tin amine as one of the products of reaction between sodium amide and trimethyl tin.

Final Reduction of Di-trimethylstannylmethane with Sodium.—With a knowledge of the action of sodium amide on trimethylstannane, it was possible to repeat the reduction of di-trimethylstannylmethane and to interpret the results with a reasonable degree of certainty. Sodium was added to a weighed quantity of the tin derivative in liquid ammonia until the end-point was reached, which was indicated by the appearance of a permanent blue color due to free metal. The data relating to this experiment are as follows: $[(CH_3)_3Sn]_2CH_2$, 1.4881 g. (4.35 m. moles); Na, 0.3505 g. (15.24 m. atoms); evolved gas, 66.95 cc. (2.99 m. moles); molecular weight of gas 15.99. On adding ammonium bromide, there was evolved a gas whose mean molecular weight was found to be 3.8.

As follows from these data, 3.5 atoms of sodium was used per mole of compound in the process of reduction. According to Equation III, 4 atoms are required. The discrepancy is doubtless due to unavoidable loss of material as a result of the volatility of trimethylstannane. The gas evolved in the course of reduction had a molecular weight corresponding closely to that of methane. The volume of methane obtained was somewhat low owing to the loss of some of the material. The gas evolved, on addition of ammonium bromide, was unquestionably hydrogen. The somewhat high value of its molecular weight was doubtless due to the presence of a small quantity of volatile tin compounds as impurities. It is almost impossible to avoid the presence of some of these compounds in the collected gases. Indeed, it was necessary to clean carefully all of the connecting tubes of the apparatus prior to carrying out an experiment; otherwise, much higher values were obtained.

The reaction evidently takes place according to Equation III. It probably occurs in two stages, as follows

$$[(CH_3)_3Sn]_2CH_2 + 2Na + NH_3 = (CH_3)_3SnNa + (CH_3)_3SnCH_3 + NaNH_2$$
$$(CH_3)_3SnCH_3 + Na + NH_3 = (CH_3)_3SnNa + CH_4 + NaNH_2$$

Summary

Di-trimethylstannylmethane, $[(CH_3)_3Sn]_2CH_2$, has been prepared and some of its properties investigated. It boils at 199–201° and has a normal molecular weight in benzene.

It has been shown that when sodium amide reacts with trimethylstannane in liquid ammonia, two reactions occur simultaneously. In one of these sodium trimethyl stannide and ammonia are formed, while in the other sodium trimethyl stannide, trimethylstannylamine and hydrogen are produced. The proportion in which these two reactions occur depends upon conditions. Sodium amide reacts with trimethyl tin to form sodium trimethyl stannide and trimethylstannylamine.

When ammonium bromide is added to a solution of sodium trimethyl stannide and sodium amide, hydrogen is evolved. For the most part, the ammonium bromide reacts with the stannide to form trimethylstannane, which in turn reacts with sodium amide, a portion to form sodium trimethyl stannide directly and another portion to form sodium trimethyl stannide, sodium trimethylstannylamine and sodium amide.

When di-trimethylstannylmethane is reduced with sodium in liquid ammonia, sodium trimethyl stannide is produced and methane is evolved.

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THE MOLECULAR WEIGHT OF CASEIN. II

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In a former publication[2] the writers have described their experiments dealing with the molecular weight of casein prepared by the method of Hammarsten and that portion of Hammarsten casein which is soluble in hot acidified 70% alcohol. The first mentioned material was found by the ultracentrifuge to be a mixture of proteins of different molecular weights, while the latter was found probably to be a distinct chemical entity having a molecular weight of 375,000.

It was pointed out in the first paper that the casein that has furnished the starting point for experimental studies in late years has been usually prepared either by the precipitation method of Hammarsten[3] or by the method of Van Slyke and Baker.[4] In the former method the precipitation was effected by the slow addition of dilute acetic acid to milk, while in the latter method normal lactic acid or a mixture of normal acetic and hydrochloric acids was recommended. The latter workers also introduced rapid agitation as a means of distributing the added acid throughout the milk.

One of the principal differences between the two methods seems to lie in the time interval during which the milk is held in a state of partial coagulation. The other principal difference is that Hammarsten redissolves the precipitated casein in dilute alkali and reprecipitates with acid several times, with the hope of removing other substances carried down during the initial precipitation; while on the other hand, Van Slyke and Baker make no attempt to remove organic impurities by reprecipitation

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[1] Fellow of the International Education Board.

[2] Svedberg, Carpenter and Carpenter, THIS JOURNAL, **52,** 241 (1930).

[3] E. Abderhalden, "Handbuch der biochemischen Arbeitsmethoden," Berlin und Wien, **1910,** Vol. II, p. 384.

[4] Van Slyke and Baker, *J. Biol. Chem.*, **35,** 127 (1918).